

Filed 2-6-04 **FILE COPY****PATENT ABSTRACTS OF JAPAN**

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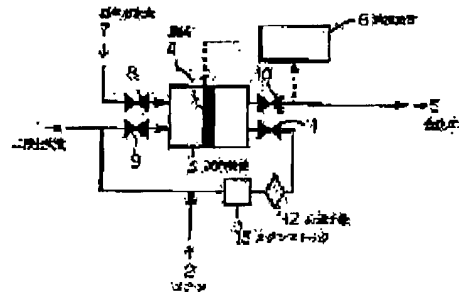
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(54) SYNTHETIC GAS PRODUCING CATALYST AND PRODUCTION USING THE SAME

(57)Abstract:

PROBLEM TO BE SOLVED: To enhance activity, to make carbon difficult to deposit and to easily remove carbon at the time of producing a synthetic gas contg. carbon monoxide and hydrogen from a gas consisting of carbon dioxide and methane by depositing palladium and rhodium on a metal oxide respective in a specified amt.

SOLUTION: Carbon dioxide 1 and methane 2 are mixed in 1:1 molar ratio and supplied to a reactor 3, a catalyst 4 prepared by depositing palladium and rhodium on a metal oxide respectively by 0.1-10wt.% is set in the reactor 3, hence the carbon dioxide 1 reacts with the methane 2, and a synthetic gas 5 contg. carbon monoxide and hydrogen is generated. The composition of the synthetic gas 5 is detected by a monitor 6 at all times. As a result, the activity of the catalyst 4 is enhanced, and elementary carbon is hardly deposited on the catalyst. If any carbon is deposited, the carbon is easily removed, and the activity of the catalyst 4 is restored.

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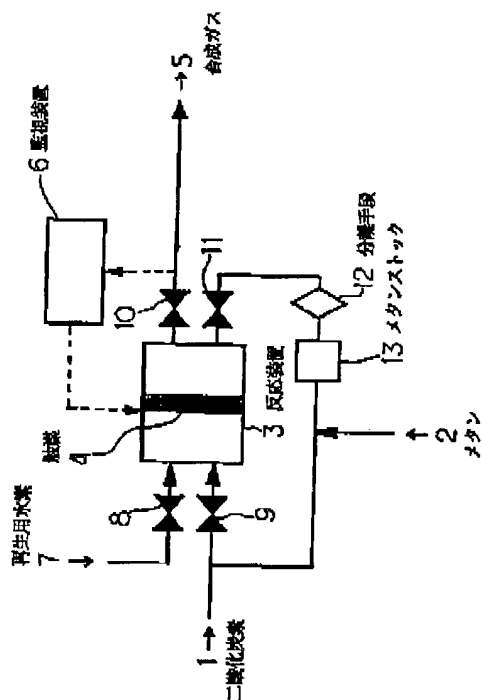
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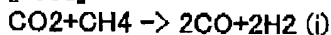
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DETAILED DESCRIPTION**[Detailed Description of the Invention]****[0001]**

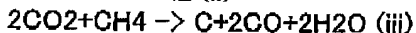
[The technical field to which invention belongs] this invention relates to the manufacture method which used the catalyst for manufacture of synthesis gas, and it. In detail, it is related with the catalyst used in case the synthesis gas containing the gas containing methane to a carbon dioxide, a carbon monoxide, and hydrogen is manufactured, and the manufacture method of synthesis gas using the catalyst.

[0002]

[Description of the Prior Art] As manufacture of the synthesis gas which used a carbon dioxide and methane as the raw material is shown in a formula (i), since it is the disappearance reaction of greenhouse gas (CO₂, CH₄), research is done in every direction by obtaining the mixed gas of CO and H₂ of the 1:1 optimal composition for the Oxo method (hydroformylation of the various olefins using the catalyst) upwards.

[0003]

As a catalyst of this above-mentioned reaction (formula (i)), the nickel-aluminum₂O₃ grade is already examined. However, although a conversion rate is not low practical in a low temperature side and, as for these, a high conversion rate is relatively obtained by the elevated-temperature side on the other hand, it becomes remarkable the following side reaction (ii) and (iii) simple substance carbon's (graphite's) depositing [to depend], degradation and deactivation of a catalyst happen, and a conversion efficiency falls with time.

[0004]

Furthermore, there were problems, like H₂ / CO ratio of the gas obtained are much less than 1 with side reaction (iii).

[0005] Invention aiming at solving such a problem is opened to JP,1-148343,A, ***** 6-503297, and JP,6-279004,A.

[0006] inside — JP,1-148343,A — the — it is related with the catalyst for synthesis gas characterized by containing the oxide of a VIII group element (the same as the eight to 10 present group to considerable and the following), and rare earth elements as an active ingredient Compared with the catalyst of nickel system for which this catalyst was used till then, there are few deposits of carbon and it characterizes by activity being high.

[0007]

[Problem(s) to be Solved by the Invention] However, if the example of the official report is seen, the H₂-/CO ratio of the synthesis gas at the time of using the 1:1 mixed gas of a carbon dioxide and methane as a raw material will be 0.89 also in the highest example, and yield's will be low, and it will have suggested that the above-mentioned side reaction (iii) is carrying out considerable grade concurrence. Moreover, also in JP,6-279004,A or a ***** No. 503297 [six to] official report, an H₂-/CO ratio is less than one, and its yield is also low.

[0008] It is difficult for the above-mentioned official report to manufacture synthesis gas continuously with the catalyst from which a deposit of the carbon of a publication tends to take place for the deactivation, and it is difficult to obtain the stable H₂-/CO ratio also in the

state where activity remains to some extent. Changing an H₂-/CO ratio sharply poses a big problem, when using the obtained synthesis gas for various raw materials.

[0009] Then, change of the H₂-/CO ratio of the synthesis gas which can remove the carbon easily even if the purpose of this invention has high activity, and carbon cannot deposit easily and deposits, as a result, enables manufacture of the synthesis gas over a long period of time, and is generated further is offering the catalyst for manufacture of the synthesis gas which gives a small reaction, and the manufacture method of synthesis gas using the catalyst.

[0010]

[Means for Solving the Problem] this invention person completed this invention, as a result of repeating various examination, in order to attain the above-mentioned purpose.

[0011] The 1st invention is a catalyst used in case the synthesis gas containing the gas containing methane to a carbon dioxide, a carbon monoxide, and hydrogen is manufactured, and relates to the catalyst for manufacture of the synthesis gas characterized by supporting palladium and a rhodium in 0.1 - 10% of the weight of the range on a metallic oxide, respectively.

[0012] The 2nd invention relates to the manufacture method of the synthesis gas characterized by using the catalyst of the 1st invention in manufacturing the synthesis gas containing the gas containing methane to a carbon dioxide, a carbon monoxide, and hydrogen.

[0013] The 3rd invention relates to the manufacture method of the synthesis gas the 2nd invention characterized by removing the simple substance carbon which deposits on a catalyst in the manufacture process of synthesis gas using hydrogen gas so that the H₂-/CO ratio (mole ratio) stabilized over the long period of time can be maintained.

[0014]

[Embodiments of the Invention] Hereafter, this invention is explained in detail.

[0015] In the catalyst of this invention, the metals supported by support are palladium and a rhodium and these are indispensable components. You may support other metals within limits which do not check the activity of palladium and a rhodium further.

[0016] The sum total of the amount of support of the palladium and the rhodium which are used for the catalyst of this invention is set as 0.1 - 10% of the weight of the range to the catalyst whole quantity, respectively. Palladium is 1.0 - 5.0 % of the weight, a rhodium is 0.5 - 5.0 % of the weight, more preferably, palladium is 1.5 - 3.1 % of the weight, and a rhodium is 0.9 - 3.0 % of the weight.

[0017] moreover, the support quantitative ratio (Pd/Rh weight ratio) of palladium and a rhodium — desirable — 0.5-4 — it is the range of 1.0-3.5 more preferably

[0018] A metallic oxide is used as support used for the catalyst of this invention. Usually, although the activated alumina (aluminum 2O₃) currently used as a catalyst support, a magnesium oxide (MgO), titanium oxide (TiO₂), a silica (SiO₂), etc. are applicable, an activated alumina (aluminum 2O₃) is desirable especially.

[0019] Manufacture of a catalyst can be conventionally performed by the well-known method. For example, the sinking-in method, a coprecipitation method, a thermal decomposition method, alligation, etc. are mentioned.

[0020] Next, the manufacture method of synthesis gas using the catalyst of this invention is explained.

[0021] As for the reaction temperature in the manufacture method of this invention, it is desirable that it is 500-1200 degrees C. It is 700-900 degrees C more preferably.

[0022] 0-20 kg/cm²G are suitable for the pressure in the manufacture method of this invention, and the range of it is 0-10 kg/cm²G preferably.

[0023] The material gas in the manufacture method of this invention is gas containing a carbon dioxide and methane. In material gas, you may contain inert gas, such as nitrogen and helium. Moreover, although it is desirable to set it as 1/1 as for the mixing ratio (CO₂/CH₄ (mole ratio)) of a carbon dioxide and methane, a reaction condition etc. may adjust a mixing ratio within the limits of 3 / 1 - 1/3. Less than [SV/h-1=60000] is suitable for the flow rate of material gas, and the range of it is not more than SV/h-1=40000 preferably. In addition, space velocity (Space Velocity) is expressed in SV.

[0024] Moreover, by the manufacture method of this invention, you may remove the simple substance carbon which deposits on a catalyst in the manufacture process of synthesis gas using hydrogen gas so that the catalyst performance stabilized over the long period of time can be maintained. For example, using the equipment shown in drawing 1, hydrogen gas can be contacted for the catalyst in a reactor, and can be carried out to it. After stopping supply of the material gas which contains a carbon dioxide and methane when an H₂-/CO ratio becomes supervising an H₂-/CO ratio with supervisory equipment although the below-mentioned example specifically explains, and separating from the set point (for example, 1/1) greatly, supplying hydrogen gas instead, making a catalyst contact and removing simple substance carbon, the aforementioned material gas is supplied again and synthesis gas is manufactured.

[0025] In manufacture of synthesis gas, it is because considerable grade concurrence is carried out [the aforementioned side reaction (ii) and (iii)] that a deposit of carbon takes place. Therefore, if such side reaction is suppressed as much as possible, a deposit of carbon can be reduced and it will enable H₂ / CO ratio to obtain about 1 synthesis gas as the result. Moreover, if depositing carbon uses an easily removable catalyst, even if carbon should deposit, it will also become sufficiently possible to use a catalyst semipermanently. Then, as a result of furthering wholeheartedly development of the catalyst for synthesis gas manufacture which can suppress such side reaction and can remove deposit carbon easily, it came to check that the catalyst of this invention is the optimal.

[0026] The catalyst of this invention arranges the low rhodium of compatibility with simple substance carbon, and the palladium which has a hydrogen radical-ized function and an occlusion function on a catalyst support. the catalyst of such this invention has an easily removable property, even if it should be markedly alike compared with the conventional catalyst, and simple substance carbon should not deposit easily and simple substance carbon should deposit. Therefore, it becomes possible to manufacture synthesis gas, suppressing a deposit of simple substance carbon by using the catalyst of this invention to the minimum. Moreover, after a prolonged reaction, even if a catalyst should deteriorate by deposit of carbon, by removing deposit carbon by the manufacture method of this invention, the performance is recovered for a short period of time, and it becomes possible to manufacture the synthesis gas by which the H₂-/CO ratio was stabilized over a long period of time.

[0027]

[Example] Hereafter, although an example explains this invention further, this invention is not limited to these.

[0028] The example of production of the catalyst of example 1 this invention is shown below. Rhodium-chloride (III) 3 hydrate and a palladium chloride (II) are melted in water, an activated alumina (aluminum 2O₃) is added and warmed in this solution, and a metal ion is infiltrated. The obtained metal ion sinking-in alumina was heat-treated under the hydrogen air current, the metal ion was returned even to the simple substance, and the alumina catalyst (Pd-Rh/aluminum 2O₃) which supported Rh for Pd 1% of the weight 3% of the weight was produced.

[0029] The mixed gas of a carbon dioxide and methane (1:1 mole ratios) was made to react in a flow rate predetermined with an ordinary pressure and the reaction temperature of 730 degrees C using Pd-Rh/aluminum 2O₃ of an example 2 - the 4 above-mentioned examples 1.

[0030] The result immediately after a reaction start is shown in Table 1. Thus, the synthesis gas a carbon monoxide and whose hydrogen are about 1:1 (mole ratio) was obtained according to the catalyst of this invention.

[0031]

[Table 1]

表1

	ガス流量 (SV/h ⁻¹)	CH ₄ 反応率 (%)	CO ₂ 反応率 (%)	H ₂ 収率 (%)	CO 収率 (%)
実施例 2	10000	96	96	94	94
実施例 3	20000	95	95	91	91
実施例 4	30000	91	92	88	89

[0032] The mixed gas of a carbon dioxide and methane (1:1 mole ratios) was made to react for a long period of time using Pd-Rh/aluminum 2O3 of the example 5 above-mentioned example 1 by the ordinary pressure, the reaction temperature of 730 degrees C, and quantity-of-gas-flow (simian virus/h -1) =10000.

[0033] A result is shown in Table 2. The synthesis gas a carbon monoxide and whose hydrogen are about 1:1 is obtained, and decline in yield is also small. Moreover, after the reaction end, although the catalyst was taken out and observed, the carbonaceous amounts of deposits were few.

[0034]

[Table 2]

表2

反応時間 (h)	CH ₄ 反応率 (%)	CO ₂ 反応率 (%)	H ₂ 収率 (%)	CO 収率 (%)
開始直後	96	96	94	94
168	93	93	91	92
336	92	93	90	91
504	88	89	86	87

[0035] Example 6 drawing 1 is explanatory drawing of the manufacture method of this example. Methane (2) is mixed with a carbon dioxide (1) by 1:1 (mole ratio), and it sends to a reactor (3). Set the catalyst (4) of this invention in a reactor (3), a carbon dioxide (1) and methane (2) are made to react efficiently, and synthesis gas (5) is generated. It enabled it to always grasp composition of synthesis gas (5) with supervisory equipment (6).

[0036] If composition should become that the range set up beforehand is likely to be exceeded, supply of a carbon dioxide (1) and methane (2) is stopped, a material gas side bulb (9) is closed, the hydrogen side bulb for reproduction (8) is opened, and the hydrogen for reproduction (7) is supplied. Moreover, a synthesis gas side bulb (10) can be closed simultaneously, and methane can be collected by opening a recovery side bulb (11). It mixes with methane (2) and this collected methane is again used as material gas. In addition, these bulb operations can be performed by electronics control.

[0037] The carbon-dioxide-methane mixed gas which made methane superfluous [size] was made to react for 168 hours using the equipment of the example 6 which set Pd-Rh/aluminum 2O3 of the example 7 aforementioned example 1 by the ordinary pressure, the reaction temperature of 730 degrees C, and quantity-of-gas-flow (SV/h -1) =10000, and simple

substance carbon was deposited intentionally. When supply of mixed gas was stopped and hydrogen was supplied instead (SV/h=30000), extremely, simple substance carbon changed to methane and it was removed in the inside of a short time (2 minutes). Carbon was not collected from the residue although the catalyst after a reaction end was dissolved from the acid. The simple substance carbon on a catalyst was sometimes clearly removed from this. [0038] The catalyst used in the example 8 above-mentioned example 7 was again used for the reaction of carbon-dioxide-methane mixed gas (1:1 mole ratios) on the same conditions as an example 5. Consequently, the same activity as reproduction before was shown as shown in Table 3.

[0039]

[Table 3]

表 3

反応時間 (h)	CH ₄ 反応率 (%)	CO ₂ 反応率 (%)	H ₂ 収率 (%)	CO 収率 (%)
開始直後	96	96	94	94
168	93	93	91	92
336	91	92	89	90
504	87	89	85	87

[0040] By the same method as example 9 example 1, Pd and Rh were supported with various ratios to the activated alumina, and the catalyst was prepared. The amount of generation of CO by each of these catalysts was relatively evaluated using TG-MS. A carbon dioxide and methane (1:1 mole ratios) were made to react in an ordinary pressure, the reaction temperature of 730 degrees C, and material gas flow rate of 100cm³/min (degree C [0], 1atm conversion) as setups. A result is shown in Table 4. In addition, CO peak intensity ratio of a mass spectrum was based on the value by the catalyst which supported only Pd.

[0041]

[Table 4]

表 4

Pd担持量 (重量%)	Rh担持量 (重量%)	Pd/Rh比	マススペクトルの COピーク強度比
0	4.0	—	0.87
0.8	3.2	1/4	1.26
1.0	3.0	1/3	1.39
1.33	2.67	1/2	1.91
2.0	2.0	1/1	3.52
2.67	1.33	2/1	3.91
3.0	1.0	3/1	4.35

3.2	0.8	4/1	2.09
4.0	0	—	1.00

[0042]

[Effect of the Invention] Even if according to this invention the activity of a catalyst should be high, simple substance carbon should hardly deposit on a catalyst and it should deposit so that clearly from the above explanation, this can be removed easily and catalytic activity can be recovered. Consequently, the synthesis gas which has stable H₂ / CO ratio can be obtained by high yield over a long period of time, and the synthesis gas used suitable for the Oxo method etc. can be obtained.

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Prior Art 2

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(12) 公開特許公報 (A)

(11) 特許出願公開番号

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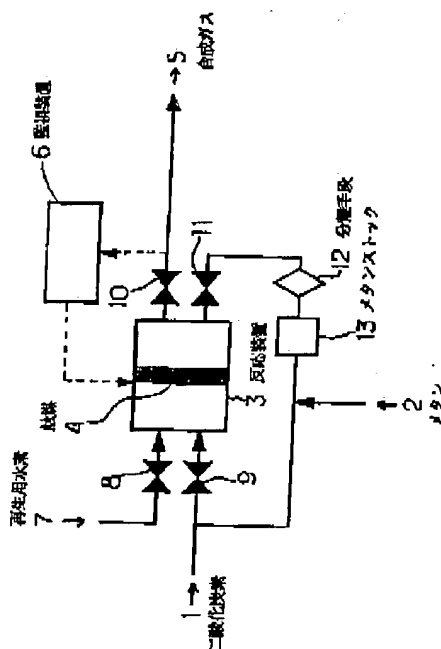
(74) 代理人 弁理士 若林 忠

(54) 【発明の名称】 合成ガスの製造用触媒及びそれを用いた製造方法

(57) 【要約】

【課題】 活性が高く、且つ炭素が析出しにくく、析出してもその炭素を容易に除去でき、その結果長期にわたる合成ガスの製造を可能とし、さらに生成する合成ガスの H_2/CO 比の変動が小さい反応を与える合成ガスの製造用触媒を提供する。

【解決手段】 一酸化炭素とメタンを含有するガスから一酸化炭素と水素を含有する合成ガスを製造する際に用いる触媒であって、パラジウムとロジウムをそれぞれ0.1～10重量%の範囲で金属酸化物上に担持したことを特徴とする合成ガスの製造用触媒、及びこの触媒を用いた合成ガスの製造方法。



(2)

特開平9-75728

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【特許請求の範囲】

【請求項1】 二酸化炭素とメタンを含有するガスから一酸化炭素と水素を含有する合成ガスを製造する際に用いる触媒であって、パラジウムとロジウムをそれぞれ0.1～10重量%の範囲で金属酸化物上に担持したことを特徴とする合成ガスの製造用触媒。

【請求項2】 二酸化炭素とメタンを含有するガスから一酸化炭素と水素を含有する合成ガスを製造するにあたり、請求項1記載の触媒を用いることを特徴とする合成ガスの製造方法。

【請求項3】 長期にわたって安定した H_2/CO 比(モル比)を維持できるように、水素ガスを用いて、合成ガスの製造過程で触媒上に析出する単体炭素の除去を行うことを特徴とする請求項2記載の合成ガスの製造方法。

【発明の詳細な説明】

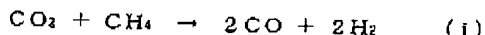
【0001】

【発明の属する技術分野】本発明は、合成ガスの製造用触媒及びそれを用いた製造方法に関する。詳しくは、二酸化炭素とメタンを含有するガスから一酸化炭素と水素を含有する合成ガスを製造する際に用いる触媒、及びその触媒を用いた合成ガスの製造方法に関する。

【0002】

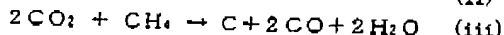
【従来の技術】二酸化炭素とメタンを原料とした合成ガスの製造は、式(i)に示すように、 O_xO 法(触媒を用いた各種オレフィンのヒドロホルミル化)に最適な1:1組成の CO と H_2 の混合ガスが得られる上に、温室効果ガス(CO_2 、 CH_4)の消滅反応であることから、各方面で研究が行われている。

【0003】



上記の本反応(式(i))の触媒としては既に $Ni-A$ 、 $12O_3$ 等が検討されている。しかし、これらは低温側では変換率が低く実用的ではなく、一方高温側では相対的に高い変換率が得られるものの、下記の副反応(ii)及び(iii)による単体炭素(グラファイト)の析出が顕著となり、触媒の劣化・失活が起こり、経時的に変換効率が低下する。

【0004】



さらに、副反応(iii)により、得られるガスの H_2/CO 比が1を大きく下回るなどの問題があった。

【0005】このような問題を解決することを目的とした発明が、特開平1-148343、特表平6-503297、及び特開平6-279004号公報に公開されている。

【0006】中でも特開平1-148343号公報は、第VIII族元素(現在の8～10族に相当、以下において同じ。)と希土類元素の酸化物とを活性成分として含有

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することを特徴とする合成ガス用触媒に関するものである。この触媒は、それまで用いられていたNi系の触媒に比べて炭素の析出が少なく、また活性も高いことが特徴とされている。

【0007】

【発明が解決しようとする課題】しかしながら、その公報の実施例を見ると、二酸化炭素とメタンの1:1混合ガスを原料とした場合の合成ガスの H_2/CO 比は、最も高い例でも0.89であり、収率も低く、上記の副反応(iii)が相当程度併発していることを示唆している。また、特開平6-279004号公報や特表平6-503297号公報においても、 H_2/CO 比は1未満であり収率も低い。

【0008】上記公報に記載の炭素の析出が起こりやすい触媒では、その失活のため継続的に合成ガスを製造することは困難であり、また活性がある程度残っている状態でも、安定した H_2/CO 比を得ることが難しい。 H_2/CO 比が大きく変動することは、得られた合成ガスを各種原料に用いる場合に大きな問題となる。

【0009】そこで本発明の目的は、活性が高く、且つ炭素が析出しにくく、析出してもその炭素を容易に除去でき、その結果長期にわたる合成ガスの製造を可能とし、さらに生成する合成ガスの H_2/CO 比の変動が小さい反応を与える合成ガスの製造用触媒、及びその触媒を用いた合成ガスの製造方法を提供することである。

【0010】

【課題を解決するための手段】本発明者は、上記の目的を達成するために種々の検討を重ねた結果、本発明を完成した。

【0011】第1の発明は、二酸化炭素とメタンを含有するガスから一酸化炭素と水素を含有する合成ガスを製造する際に用いる触媒であって、パラジウムとロジウムをそれぞれ0.1～10重量%の範囲で金属酸化物上に担持したことを特徴とする合成ガスの製造用触媒に関する。

【0012】第2の発明は、二酸化炭素とメタンを含有するガスから一酸化炭素と水素を含有する合成ガスを製造するにあたり、第1の発明の触媒を用いることを特徴とする合成ガスの製造方法に関する。

【0013】第3の発明は、長期にわたって安定した H_2/CO 比(モル比)を維持できるように、水素ガスを用いて、合成ガスの製造過程で触媒上に析出する単体炭素の除去を行うことを特徴とする第2の発明の合成ガスの製造方法に関する。

【0014】

【発明の実施の形態】以下、本発明を詳細に説明する。

【0015】本発明の触媒において、担体に担持される金属はパラジウムとロジウムであり、これらが必須成分である。パラジウムとロジウムの活性を阻害しない範囲内で、その他の金属をさらに担持してもよい。

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【0016】本発明の触媒に用いるパラジウムとロジウムの担持量の合計は、触媒全量に対して、それぞれ0.1～10重量%の範囲に設定する。好ましくは、パラジウムが1.0～5.0重量%、ロジウムが0.5～5.0重量%であり、より好ましくは、パラジウムが1.5～3.1重量%、ロジウムが0.9～3.0重量%である。

【0017】また、パラジウムとロジウムの担持量比(Pd/Rh重量比)は、好ましくは0.5～4、より好ましくは1.0～3.5の範囲である。

【0018】本発明の触媒に用いる担体としては金属酸化物を用いる。通常触媒担体として使用されている活性アルミナ(Al_2O_3)、酸化マグネシウム(MgO)、酸化チタン(TiO_2)、シリカ(SiO_2)等が適用できるが、中でも活性アルミナ(Al_2O_3)が好ましい。

【0019】触媒の調製は、従来公知の方法で行うことができる。例えば、含浸法、共沈法、熱分解法、混合法等が挙げられる。

【0020】次に、本発明の触媒を用いた合成ガスの製造方法について説明する。

【0021】本発明の製造方法における反応温度は500～1200℃であることが好ましい。より好ましくは700～900℃である。

【0022】本発明の製造方法における圧力は、0～20 kg/cm²Gが適当であり、好ましくは0～10 kg/cm²Gの範囲である。

【0023】本発明の製造方法における原料ガスは、一酸化炭素とメタンを含有するガスである。原料ガスには、窒素、ヘリウム等の不活性ガスを含有していてもよい。また、一酸化炭素とメタンの混合比(CO_2/CH_4 (モル比))は、1/1に設定することが望ましいが、反応条件等によっては、3/1～1/3の範囲内で混合比を調整してもよい。原料ガスの流量は、 $SV/h^{-1} = 60000$ 以下が適当であり、好ましくは $SV/h^{-1} = 40000$ 以下の範囲である。なお、SVとは空間速度(Space Velocity)を表す。

【0024】また、本発明の製造方法では、長期にわたって安定した触媒性能を維持できるように、水素ガスを用いて、合成ガスの製造過程で触媒上に析出する単体炭素の除去を行ってもよい。例えば、図1に示す装置を用いて、反応装置内の触媒に水素ガスを接触させて行うことができる。具体的には後述の実施例で説明するが、 H_2/CO 比を監視装置により監視し、 H_2/CO 比が設定値(例えば1/1)を大きく外れそうになった際に、一酸化炭素とメタンを含有する原料ガスの供給を止め、代わりに水素ガスを供給して触媒に接触させて単体炭素の除去を行った後に、再び前記の原料ガスを供給して合成

ガスを製造する。

【0025】合成ガスの製造において、炭素の析出が起こるのは、前記副反応(ii)及び(iii)が相当程度併発していることが原因である。従って、これらの副反応を可能な限り抑制すれば、炭素の析出を減らすことができ、その結果として H_2/CO 比がほぼ1の合成ガスを得ることが可能となる。また、万一炭素が析出して、析出した炭素が容易に除去できる触媒を用いれば、半永久的に触媒を用いることも十分可能となる。そこで、このような副反応を抑えることができ、且つ析出炭素を容易に除去することができる合成ガス製造用触媒の開発を鋭意進めた結果、本発明の触媒が最適であることを確認するに至った。

【0026】本発明の触媒は、単体炭素との親和性の低いロジウムと、水素ラジカル化機能と吸蔵機能を有するパラジウムとを触媒担体上に配置している。このような本発明の触媒は、従来の触媒に比べ格段に単体炭素が析出しにくく、また、万一単体炭素が析出して也容易に除去することができる性質を持っている。したがって、本発明の触媒を用いることによって、単体炭素の析出を最小限に抑えながら合成ガスを製造することが可能となり、また、長期間の反応後、万一炭素の析出によって触媒が劣化した場合でも、本発明の製造方法により析出炭素の除去を行うことにより、短期間にその性能が回復し、 H_2/CO 比が安定した合成ガスを長期にわたって製造することが可能となる。

【0027】

【実施例】以下、本発明を実施例によりさらに説明するが、本発明はこれらに限定するものではない。

【0028】実施例1

本発明の触媒の作製例を以下に示す。塩化ロジウム(II)三水合物と塩化パラジウム(II)とを水にとかし、この溶液に活性アルミナ(Al_2O_3)を加えて加温し、金属イオンを含浸させる。得られた金属イオン含浸アルミナを水素気流下で加熱処理し、金属イオンを単体にまで還元し、Pdを3重量%、Rhを1重量%担持したアルミナ触媒(Pd-Rh/ Al_2O_3)を作製した。

【0029】実施例2～4

上記実施例1のPd-Rh/ Al_2O_3 を用いて、常圧、反応温度730℃で所定の流量において一酸化炭素とメタン(1:1モル比)の混合ガスを反応させた。

【0030】反応開始直後の結果を表1に示す。このように、本発明の触媒により一酸化炭素と水素がほぼ1:1(モル比)である合成ガスが得られた。

【0031】

【表1】

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表1

	ガス流量 (SV/h ⁻¹)	CH ₄ 反応率 (%)	CO ₂ 反応率 (%)	H ₂ 収率 (%)	CO収率 (%)
実施例2	10000	96	96	94	94
実施例3	20000	95	95	91	91
実施例4	30000	91	92	88	89

【0032】実施例5

上記実施例1のPd-Rh/Al₂O₃を用いて、常圧、反応温度730℃、ガス流量(SV/h⁻¹)=10000で、二酸化炭素とメタン(1:1モル比)の混合ガスを長期間反応させた。

【0033】結果を表2に示す。二酸化炭素と水素がほ

ぼ1:1である合成ガスが得られ、収率の低下も小さい。また、反応終了後、触媒を取り出して観察したが、炭素の析出量はわずかであった。

【0034】

【表2】

表2

反応時間 (h)	CH ₄ 反応率 (%)	CO ₂ 反応率 (%)	H ₂ 収率 (%)	CO収率 (%)
開始直後	96	96	94	94
168	93	93	91	92
336	92	93	90	91
504	88	89	86	87

【0035】実施例6

図1は、本実施例の製造方法の説明図である。二酸化炭素(1)とメタン(2)を1:1(モル比)で混合し反応装置(3)へ送る。反応装置(3)には本発明の触媒(4)をセットし、二酸化炭素(1)とメタン(2)とを効率よく反応させ、合成ガス(5)を発生させる。合成ガス(5)の組成は、監視装置(6)で常に把握できるようにした。

【0036】万一、組成が予め設定している範囲を超えそうになった場合は、二酸化炭素(1)とメタン(2)の供給を止め、原料ガス側バルブ(9)を閉じ、再生用水素側バルブ(8)を開いて再生用水素(7)を供給する。また、同時に合成ガス側バルブ(10)を閉じ、回収側バルブ(11)を開くことによってメタンを回収することができる。この回収されたメタンは、メタン(2)と混合し、再び原料ガスとして用いる。なお、これらのバルブ操作は電子制御で行うことができる。

【0037】実施例7

前記実施例1のPd-Rh/Al₂O₃をセットした実施例6の装置を用いて、メタンを大過剰とした二酸化炭素-メタン混合ガスを、常圧、反応温度730℃、ガス流量(SV/h⁻¹)=10000で168時間反応させ、意図的に単体炭素を析出させた。混合ガスの供給を中止し、代わりに水素を供給(SV/h⁻¹=30000)したところ、極めて短時間(2分)のうちに単体炭素がメタンに変化し除去された。反応終了後の触媒を酸で溶解したが、その残渣から炭素は回収されなかった。このことより、触媒上の単体炭素が除去されたことは明らかである。

【0038】実施例8

上記実施例7で用いた触媒を、実施例5と同じ条件で再び二酸化炭素-メタン混合ガス(1:1モル比)の反応に用いた。その結果、表3に示す通り、再生前と同様な活性を示した。

【0039】

【表3】

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表3

反応時間 (h)	CH ₄ 反応率 (%)	CO ₂ 反応率 (%)	H ₂ 収率 (%)	CO収率 (%)
開始直後	96	96	94	94
168	98	93	91	92
336	91	92	89	90
504	87	89	85	87

【0040】実施例9

実施例1と同様な方法により、PdとRhを種々の比で活性アルミナに担持し、触媒を調製した。これらの触媒の各々によるCOの生成量を、TG-MSを用いて相対的に評価した。設定条件として常圧、反応温度730℃、原料ガス流量100cm³/min (0℃、1atm換算)

において、二酸化炭素とメタン(1:1モル比)を反応させた。結果を表4に示す。なお、マスペクトルのCOピーク強度比は、Pdのみを担持した触媒による値を基準とした。

【0041】

【表4】

表4

Pd担持量 (重量%)	Rh担持量 (重量%)	Pd/Rh比	マスペクトルの CO ₂ ピーク強度比
0	4.0	—	0.87
0.8	3.2	1/4	1.26
1.0	3.0	1/3	1.39
1.33	2.67	1/2	1.91
2.0	2.0	1/1	3.52
2.67	1.33	2/1	3.91
3.0	1.0	3/1	4.35
3.2	0.8	4/1	2.09
4.0	0	—	1.00

【0042】

【発明の効果】以上の説明から明らかなように本発明によれば、触媒の活性が高く、且つ触媒上には単体炭素がほとんど析出せず、また万一析出しても容易にこれを除去して触媒活性を回復させることができる。その結果、安定したH₂/CO比を有する合成ガスを長期にわたって高収率で得ることができ、Ox法等に好適に用いられる合成ガスを得ることができる。

【図面の簡単な説明】

【図1】本発明の合成ガスの製造方法の説明図である。

【符号の説明】

- 1 二酸化炭素 (CO₂)
- 2 メタン (CH₄)
- 3 反応装置
- 4 触媒
- 5 合成ガス

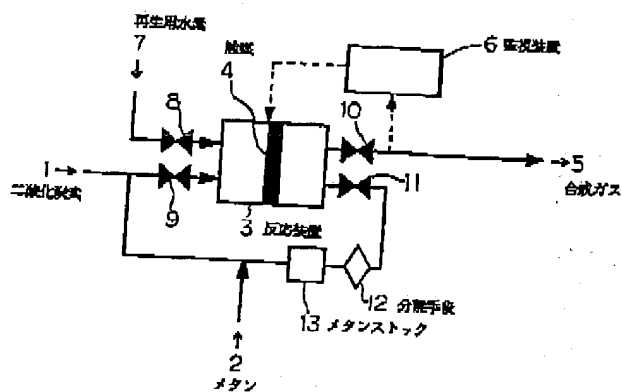
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- 6 監視装置
7 再生用水素
8 再生用水素側バルブ
9 原料ガス側バルブ

- 10 合成ガス側バルブ
11 回収側バルブ
12 分離手段
13 メタンストック

【図1】



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JAPANESE

[JP,08-175805,A]

08-175805

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE
INVENTION TECHNICAL PROBLEM MEANS EXAMPLE DESCRIPTION OF DRAWINGS
DRAWINGS

[Translation done]

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CLAIMS**[Claim(s)]**

[Claim 1] A manufacturing method of hydrogen characterized by using a catalyst which supported an active metal to alumina content support which has aluminum³⁺ of 5 coordination in a method of contacting gas containing methane and a carbon dioxide for a catalyst, and manufacturing a carbon monoxide and hydrogen.

[Claim 2] A manufacturing method of a carbon monoxide characterized by using a catalyst which supported an active metal to alumina content support which has aluminum³⁺ of 5 coordination in a method of contacting gas containing methane and a carbon dioxide for a catalyst, and manufacturing a carbon monoxide and hydrogen.

[Claim 3] A manufacturing method of hydrogen according to claim 1 to which a catalyst contains an alumina which has aluminum³⁺ of 5 coordination 0.1 to 50% of the weight in alumina content support.

[Claim 4] A manufacturing method of a carbon monoxide according to claim 2 with which a catalyst contains an alumina which has aluminum³⁺ of 5 coordination 0.1 to 50% of the weight in alumina content support.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the method of manufacturing a useful carbon monoxide and hydrogen (it abbreviating to "synthesis gas" below) industrially, using the methane which is the principal component of natural gas, and the carbon dioxide used as the main causative agents of global warming.

[0002]

[Description of the Prior Art] In recent years, since carbon dioxide gas is the main causative agent of global warming, let it be the technical problem that the cutback of blowdowns and a deployment are pressing. For this reason, the chemical conversion methods, such as electric reduction of carbon dioxide gas, the photosynthesizing method, and a contact hydrogen reduction method, are considered. There are very few examples of a report about the method of manufacturing synthesis gas useful as a raw material at the time of compounding various organic compounds by the hydroformylation from methane and a carbon dioxide among these, and the contact process (React.Kinet.catal., 24,253 (1984) and the collection of the 68th catalyst (debate A) drafts, 3H327 (1991)) which used 8 group transition-metals support catalyst for an alumina or silica support is known slightly.

[0003] However, the catalyst which supported noble metals is expensive and economically disadvantageous. Moreover, it has catalytic activity and a life equivalent to noble metals, and since the carbon deposit inclination of a nickel catalyst is strong, it has the problem that lowering of activity tends to take place also in cheaper 8 group transition metals.

[0004]

[Problem(s) to be Solved by the Invention] Therefore, from the gas containing methane and a carbon dioxide, this invention controls a deposit of carbon and aims at offering the method of manufacturing a carbon monoxide and hydrogen efficiently.

[0005]

[Means for Solving the Problem] In a method of this invention person contacting gas containing methane and a carbon dioxide for a catalyst in such the actual condition as a result of inquiring wholeheartedly, and manufacturing a carbon monoxide and hydrogen, if an alumina content catalyst which has aluminum³⁺ of 5 coordination is used, since a deposit of carbon is controlled and lowering of catalytic activity cannot take place easily, it came to complete a header and this invention for the ability of hydrogen and a carbon monoxide to be manufactured efficiently.

[0006] That is, this invention offers a manufacturing method of hydrogen characterized by using a catalyst which supported an active metal for an alumina which has aluminum³⁺ of 5 coordination to content support in a method of contacting gas containing methane and a carbon dioxide for a catalyst, and manufacturing a carbon monoxide and hydrogen. Moreover, this invention offers a manufacturing method of a carbon monoxide characterized by using a catalyst which supported an active metal for alumina content support which has aluminum³⁺ of 5 coordination in a method of contacting gas containing methane and a carbon dioxide for a catalyst, and manufacturing a carbon monoxide and hydrogen.

[0007] As methane used by this invention, any of methane independence and methane content gas are sufficient. As methane content gas, natural gas and substitute natural gas are

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mentioned, for example, and unsaturated hydrocarbon; diacid carbonizing-ized hydrogen, such as saturated hydrocarbon; ethylene, such as ethane and a propane, a propene, and a butene, a hydrogen sulfide of a minute amount, 10-40-mol % of hydrogen, 1-20-mol % of a carbon monoxide, nitrogen, air, or a steam other than methane may be included.

[0008] In this invention, 0.05-25, and that it is especially 0.1-20, and also 0.2-10 have [a mole ratio of methane used as a raw material, and a carbon dioxide] a desirable mole ratio of methane/carbon dioxide. If an amount of a carbon dioxide which a mole ratio of methane/carbon dioxide recycles less than by 0.05 increases, yield of hydrogen decreases and 25 is exceeded, sufficient carbon monoxide generation rate will no longer be obtained, and a carbon deposit will also become and uneconomical.

[0009] A catalyst used by this invention supports an active metal to alumina content support which has aluminum³⁺ of 5 coordination, it is known that 3 kinds of aluminum³⁺ of 4 coordination, 5 coordination, and 6 coordination exists in an amorphous alumina — *** (Dupree, Journal De Physique, C8,113 (1985)) — an alumina used by this invention may contain an alumina which otherwise has aluminum³⁺ of 4 or 6 coordination that what is necessary is just to include an alumina which has aluminum³⁺ of 5 coordination.

[0010] Among alumina content support, especially although especially the blending ratio of coal of an alumina that has aluminum³⁺ of 5 coordination is not restricted, it is desirable in alumina content support that it is 1 - 50 % of the weight 0.1 to 70% of the weight. At less than 0.1 % of the weight, it is difficult to adjust what depressor effect of sufficient carbon deposit is not acquired, but exceeds 70 % of the weight.

[0011] In addition, a coordination condition of aluminum³⁺ can be known by using the ²⁷aluminum-solid-state NMR.

[0012] an alumina which has aluminum³⁺ of 5 coordination — the usual grinding method and HITOSSHOKU — law, a sol gel process of an organoaluminum compound, etc. — it can manufacture — for example, Journal of It can manufacture according to Catalysis, 133,263 (1992) and Chem.Mater., and a method indicated by 5 and 1204 (1993).

[0013] after [namely,] carrying out day boiling of the sodium-aluminate aqueous solution, and centrifugal separation's separating enough and washing obtained settlements as a grinding method — a jib — a site is obtained, next, this jib — method: which obtains an alumina which grinds with a ball mill for 50 to 300 hours, and has aluminum³⁺ of 5 coordination after calcinating a site at 300-600 degrees C for 0.1 to 5 hours — a jib — a method of carrying out hydrothermal synthesis of the mixture of a site and water, obtaining boehmite, and obtaining an alumina which grinds with a ball mill at 50-500 degrees C next for 0.1 to 100 hours, and has aluminum³⁺ of 5 coordination etc. is mentioned.

[0014] Moreover, as a sol gel process, add water to a mixed solution of a sec-butyl alcohol solution of aluminum-tri sec butoxide, and a urea solution which dissolved in sec-butyl alcohol, and a sol is made to generate, after aging, ammonium bicarbonate is added at a room temperature and gel is settled. In order to remove unreacted aluminum butoxide, sec-butyl alcohol washes obtained gel enough, gel is dried and calcinated after that, and a method of obtaining an alumina which has aluminum³⁺ of 5 coordination is mentioned.

[0015] Since what alumina content support used by this invention may contain metallic oxides, such as a silica besides an alumina, a zirconia, NIOBIA, a titania, crystalline alumina silicate, a calcium oxide, a magnesium oxide, and a barium oxide, and contains especially a calcium oxide, a magnesium oxide, and a barium oxide can control a carbon deposit to validity more, it is desirable. Although especially the blending ratio of coal of these inorganic oxides is not restricted, it is desirable in alumina content support that it is 0.1 - 40 % of the weight.

[0016] Although not restricted especially as an active metal supported to alumina content support, 8 group transition metals, such as nickel, a ruthenium, a rhodium, iridium, and cobalt, are especially desirable, for example, and nickel is desirable from a point of cost. Moreover, an oxide of these metals may be used.

[0017] As for especially an active metal supported to alumina content support, it is desirable to contain 1.0 to 50% of the weight 0.01 to 70% of the weight by metal conversion in [all] a catalyst. Even if an invert ratio of carbon dioxides enough at less than 0.01 % of the weight is

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not obtained but it exceeds 70 % of the weight, improvement in an invert ratio to the extent that it expects is not obtained.

[0018] Especially a method of making alumina content support support an active metal is not restricted, for example, can use well-known methods, such as an impregnation method, a sol gel process, and physical alligation.

[0019] For example, alumina molding which has aluminum³⁺ of 5 coordination is immersed in an aqueous solution containing metals, such as nickel salt. How to return after desiccation and baking; Add ammonium to an aqueous solution which dissolved an aluminum salt, and precipitation of an aluminum hydroxide is formed. A method which is immersed in an aqueous solution containing metals, such as nickel salt, and returns after desiccation and baking after drying and calcinating obtained gel; physical mixing of a nickel oxide and the alumina which has aluminum³⁺ of 5 coordination is carried out, and a method of returning is mentioned after desiccation and baking.

[0020] In these methods, a catalyst may be performed after immobilization and desiccation and within a reactor that what is necessary is just to carry out, using reducing gas as a method of returning a catalyst.

[0021] As reducing gas, pure hydrogen, hydrogen and a steam, and a carbon monoxide can be used, hydrogen gas, or hydrogen and steam gas is desirable, and it is desirable to use especially hydrogen gas. Moreover, although reduction can perform methane and a carbon dioxide with reaction temperature at a time of making a catalyst contact, it is desirable to carry out at about 200-800 degrees C so that an active metal made to support may not condense.

[0022] A manufacturing method of this invention is performed by contacting gas which contains methane and a carbon dioxide for a catalyst acquired by doing in this way. As for especially reaction temperature, at this time, it is desirable that it is 400-900 degrees C 300-1000 degrees C. If sufficient invert ratio of methane and a carbon dioxide is not obtained at less than 300 degrees C but reaction temperature exceeds 1000 degrees C, lowering of activity by sintering of a catalyst will arise. Moreover, as for especially reaction pressure, it is desirable for it not to be restricted but to carry out with ordinary pressure - 20 atmospheric pressure, especially ordinary pressure - 10 atmospheric pressure. Furthermore, it is desirable GHSV500-500,000h⁻¹ and to supply especially material gas at the rate of 1,000-300,000h⁻¹. If a generation rate of a carbon monoxide is small and exceeds 500,000h⁻¹, an invert ratio of a raw material falls and it is not economical at less than [500h -] one.

[0023] As a reaction method, especially if a catalyst and a raw material can contact efficiently, it will not be restricted, for example, it can be made to react in the fixed bed, the fluid bed, and the moving bed.

[0024]

[Effect of the Invention] Since according to this invention a deposit of carbon is controlled and catalytic activity moreover cannot fall easily by using the alumina content catalyst which has aluminum³⁺ of 5 coordination in the method of contacting the gas containing methane and a carbon dioxide for a catalyst, and manufacturing a carbon monoxide and hydrogen, the invert ratio of methane and a carbon monoxide is high, and hydrogen and a carbon monoxide can be obtained efficiently.

[0025]

[Example] Hereafter, although an example explains this invention still more concretely, this is only instantiation and does not restrict this invention.

[0026] example of reference 1 alumina preparation: — the white sediment which will boil an one-mol sodium-aluminate aqueous solution for one day, was made to hydrolyze, and was obtained — centrifugal separation — carrying out — washing — a jib — the site was obtained, next, this jib — 500 degrees C of sites were calcinated for 1 hour, and the comparison alumina C was obtained. The alumina A which furthermore grinds this alumina C with a ball mill for 125 hours, and has 5 coordination aluminum³⁺ was obtained, moreover, a jib — hydrothermal synthesis of the mixture of 10ml of water was carried out to site 5g for two days at 350 degrees C among the autoclave, and boehmite was obtained. Next, after

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calcinating this at 400 degrees C for 1 hour, the alumina B which carries out grinding processing with a ball mill for 350 hours, and has 5 coordination aluminum³⁺ was obtained. Furthermore, boehmite was calcinated at 600 degrees C for 1 hour, and the comparison alumina D was obtained.

[0027] The coordination number was measured by the ²⁷aluminum-solid-state NMR. For 65.6 ppm and 5 coordination, 38.3 ppm and 6 coordination are [the chemical shift of ²⁷aluminum to 4 coordination] 11.4 ppm. It could specify and the trial calculation of the content was made by the intensity ratio. The content of aluminum³⁺ which has 4 coordination of alumina A-D, 5 coordination, or 6 coordination was shown in a table 1, and the ²⁷aluminum-solid-state NMR spectrum was shown in drawing 1 ~4.

[0028] Preparation of the example [of reference] 2 catalyst A: The catalyst A which consists of 10 % of the weight of nickel and 90 % of the weight of aluminas was acquired by calcinating alumina 4.6g which carried out making tablet molding, ground alumina A powder, and carried out the particle size regulation to 20-30 meshes at 500 degrees C for 1 hour, after being immersed in the aqueous solution which dissolved 2.3g of nickel nitrate 6 hydrates in 9ml of water for 3 hours and drying at 110 degrees C subsequently overnight.

[0029] Preparation of the example [of reference] 3 catalyst B: The catalyst B which consists of 2 % of the weight of rhodiums and 98 % of the weight of aluminas was acquired like the example 2 of reference except having used nitric-acid rhodium 6 hydrate instead of nickel nitrate 6 hydrate.

[0030] Preparation of the example [of reference] 4 catalyst C: Alumina B After having hydrolyzed 4.6g in the ammonium-chloride aqueous solution after being immersed in the aqueous solution which dissolved 2.3g of ruthenium chloride 3 hydrates in 9ml of water for 3 hours, and drying at desiccation and 110 more degrees C with a room temperature subsequently for 3 hours overnight, the catalyst C which consists of 2 % of the weight of rutheniums and 98 % of the weight of aluminas was acquired by calcinating at 500 degrees C for 1 hour.

[0031] Preparation of the example [of reference] 5 catalyst D: Alumina B which carried out the particle size regulation to 20-30 meshes It dried at 110 degrees C overnight, and 4.2g was calcinated at 600 more degrees C for 2 hours, after being immersed in the aqueous solution which dissolved 2.5g of magnesium acetate 4 hydrates in 8ml of water for 3 hours. The catalyst D which consists of 10 % of the weight of nickel, 27 % of the weight of magnesium oxides, and 63 % of the weight of aluminas was acquired by calcinating 4.6g of obtained baking objects at 500 degrees C for 1 hour, after being immersed in the aqueous solution which dissolved 2.3g of nickel nitrate 6 hydrates in 5ml of water for 3 hours and drying at 110 degrees C subsequently overnight.

[0032] Preparation of the example [of reference] 5 catalyst E: Instead of magnesium acetate 4 hydrate, the catalyst E which consists of 10 % of the weight of nickel, 27 % of the weight of calcium oxides, and 63 % of the weight of aluminas was acquired like the example 5 of reference except having used the calcium oxide.

[0033] Preparation of the example [of reference] 6 catalyst F: Alumina C which carried out the particle size regulation to 20-30 meshes The catalyst F which consists of 10 % of the weight of nickel and 90 % of the weight of aluminas was acquired by drying at 110 degrees C overnight and calcinating 14g at 500 more degrees C for 1 hour, after being immersed in the aqueous solution which dissolved 6.9g of nitric-acid rhodium 6 hydrates in 20ml of water for 3 hours.

[0034] Preparation of the example [of reference] 7 catalyst G: Alumina C which carried out the particle size regulation to 20-30 meshes The catalyst G which consists of 2 % of the weight of rhodiums and 98 % of the weight of aluminas was acquired by drying at 110 degrees C overnight and calcinating 14g at 500 more degrees C for 1 hour, after being immersed in the aqueous solution which dissolved 6.9g of nickel nitrate 6 hydrates in 20ml of water for 3 hours.

[0035] Preparation of the example [of reference] 8 catalyst H: Alumina D which carried out the particle size regulation to 20-30 meshes The catalyst F which consists of 10 % of the

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weight of nickel and 90 % of the weight of aluminas was acquired by drying at 110 degrees C overnight and calcinating 14g at 500 more degrees C for 1 hour, after being immersed in the aqueous solution which dissolved 6.9g of nickel nitrate 6 hydrates in 20ml of water for 3 hours.

[0036] Preparation of the example [of reference] 9 catalyst I: Alumina D The catalyst F which consists of 10 % of the weight of nickel and 90 % of the weight of aluminas was acquired by drying at 110 degrees C overnight and calcinating 14g at 500 more degrees C for 1 hour, after being immersed in the aqueous solution which dissolved 6.9g of nickel nitrate 6 hydrates in 20ml of water for 3 hours.

[0037] After filling up the container made from alpha-alumina in the diameter of 8mm of one to examples 1-5 and example of comparison 4 differential thermal analyzer (DTA-500, product made from the SEIKO electronic industry) with 20mg of catalysts and equipping on a sample cell, reduction processing was performed at 600 degrees C under the hydrogen ambient atmosphere for 1 hour, and temperature up was carried out to 900 degrees C under the helium ambient atmosphere after that. Next, it replaced with helium, the mixed gas of a carbon dioxide (47-mol %), methane (47-mol %), and nitrogen (six-mol %) was supplied by 40 ml/min, holding at 900 degrees C, (GHSV150,000hr⁻¹), and hydrogen and a carbon monoxide were obtained. Gas-chromatography analysis of the reaction generation gas was carried out, and the invert ratio and carbon are recording speed of methane and a carbon dioxide were computed by the degree type. A result is shown in a table 1.

[0038]

[Equation 1]

$$\text{CH}_4\text{転化率 (\%)} = \frac{\text{供給CH}_4\text{のモル数} - \text{出口CH}_4\text{のモル数}}{\text{供給CH}_4\text{のモル数}} \times 100$$

$$\text{CO}_2\text{転化率 (\%)} = \frac{\text{供給CO}_2\text{のモル数} - \text{出口CO}_2\text{のモル数}}{\text{供給CO}_2\text{のモル数}} \times 100$$

$$\text{炭素生成速度 (\mu g / hr}^{-1} \cdot g^{-1}) = \frac{\text{単位時間当たりの炭素生成重量}}{\text{触媒重量}}$$

[0039]

[A table 1]

	触媒	Al ³⁺ 配位数分布 4/5/6 (%/%/%)	CH ₄ 転化率 (%)	CO ₂ 転化率 (%)	収率 (%)				炭素生成速度 ($\mu\text{g} \cdot \text{hr}^{-1} \cdot \text{g}^{-1}$)
					CO	H ₂	C	H ₂ O	
実施例 1	A	20/5/75	48	48	49.7	50	0.3	0	0.18
実施例 2	B	20/5/75	44	45	49.9	50	0.1	1	0.06
実施例 3	C	25/25/50	43	50	49.8	50	0.2	0	0.08
実施例 4	D	25/25/50	47	48	49.9	50	0.1	0	0.08
実施例 5	E	25/25/50	46	47	49.8	50	0.2	0	0.06
比較例 1	F	30/0/70	31	37	49.3	50	6.7	0	4.02
比較例 2	G	30/0/70	34	39	49.2	48	0.8	2	0.48
比較例 3	H	25/0/75	30	35	48.5	50	4.5	0	2.70
比較例 4	J	25/0/75	32	37	49.9	49	0.0	1	0.54

[0040] When alumina content catalyst A-E containing 5 coordination aluminum³⁺ is used, compared with the case of comparison catalyst F-I, the invert ratio of methane and a carbon

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dioxide is high, and the result of a table 1 shows that the carbon deposit on a catalyst is decreasing remarkably.

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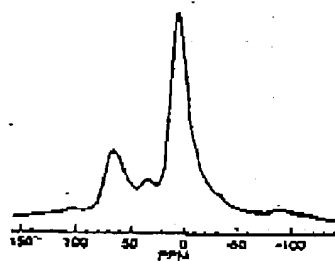
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Drawing selection drawing 1 

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